SYNTHESIS AND CHARACTERIZATION OF Al-4.5%Cu ALLOY POWDER USING MECHANICAL ALLOYING

A THESIS SUBMITTED IN PARTIAL FULLFILLMENT

OF THE REQUIREMENT FOR THE DEGREE OF

Bachelor of Technology

In

Metallurgical and Materials Engineering

By

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KISHORE VADLAMOODI (108MM030)

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Certificate

This is to certify that the thesis entitled "Synthesis and Characterization of Al-4.5%Cu powder using Mechanical Alloying" being submitted by Kshitiz Anand (108MM038), Kishore Vadlamoodi(108MM030), Seshadri Deb Roy(108MM050) for the partial fulfillment of the requirements of Bachelor of Technology degree in Metallurgical and Materials engineering is a bona fide thesis work done by them under my supervision during the academic year 2011-2012, in the Department of Metallurgical and Materials Engineering, National Institute of Technology Rourkela, India.

The results presented in this thesis have not been submitted elsewhere for the award of any other degree or diploma.

Date:

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Abstract

The present work aims to improve the mechanical properties of Duralumin (Al-4.5 wt. % Cu) alloy produced by mechanical alloying and consolidated using conventional isotactic hydraulic compressor. A uniform dispersion of SiC and TiO_2 reinforcements tends to improve the mechanical properties of the present alloys. The current alloys show extraordinary hardness values which are 1-1.5 times higher than the conventional duralumin alloys. For this purpose, pure elemental powders of Al and Cu were blended and milled in a planetary ball mill and sintered at 550°C for 1 hour in Argon atmosphere. XRD and SEM of samples collected at different stages during milling and after sintering were done to determine the phase evolution and microstructural morphology of the current alloys. The crystallite size, lattice strain and lattice parameters were analyzed by Williamson-Hall method. The crystallite size decreases rapidly up to 7 hours of milling and becomes almost constant with further milling. Addition of SiC (5 and 10 vol. %) and TiO_2 (5 and 10 vol. %) as reinforcements in the matrix improves the hardness. Addition of SiC reinforcement leads to better dispersion than TiO_2 as evident from the hardness values. This is due to the higher modulus of elasticity of SiC which is almost double than that of TiO_2.

Contents

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1 Introduction

Duralumin (Al-4.5%Cu) is a strong, hard, lightweight alloy of aluminum, widely used in aircraft construction. Duralumin alloys are relatively soft, ductile, and workable in the normal state; they may be rolled, forged, extruded, or drawn into a variety of shapes and products. Their light weight and consequent high strength per unit weight compared to steel suit them for aircraft construction. Addition of reinforcements like SiC or TiO_2 to the base composition Al-4.5%Cu increases the strength and other mechanical properties. As the densities of the reinforcements and the base alloy compositions are different, it is very difficult to produce the alloy by common techniques like rapid solidification or melting. Mechanical alloying (MA), on the other hand, being a solid-state powder processing technique ensures a uniform dispersion of reinforcement particles throughout the matrix. Moreover alloy produced via MA are free from defects arising due to the high temperature and liquid phases, for instance formation of cracks at the reinforcement /Al-Cu interface, agglomeration of reinforcement particles at the grain boundaries of the matrix and also the degradation of mechanical properties due to the formation of Al_4C_3.

In the present work improved mechanical property of Al-4.5%Cu matrix reinforced with SiC (5 and 10 vol. %) and TiO_2 (5 and 10 vol. %) has been analyzed. In short the aim of the work is:

- To produce uniform dispersion hardened Al-4.5%Cu alloys by consolidation of milled alloy powders.
- Characterization of the mechanically alloyed powders at different stages of milling as well as consolidated alloys using XRD and SEM.
- To calculate and compare the particle size, lattice strain and measuring the hardness values of the different alloys produced.

The present thesis has been presented in five different chapters. Following a general introduction, here, in Chapter 1; Chapter 2 provides a literature review of the present status of understanding in the field of Aluminium alloys produced by mechanical alloying. The entire scheme of experimental studies including equipment used, their description, operating parameters, collection and analysis of data are presented in Chapter 3 followed by results and discussion in Chapter 4. Finally the thesis ends with Chapter 5 which provides summary of present study and future scope of study. References are provided after Chapter 5.

2. Literature Survey

Various research have showed that the structure and constitution of advanced materials can be better controlled by processing them under non-equilibrium (or far from equilibrium) conditions [2]. Amongst many such processes, which are in commercial use, rapid solidification from the liquid state [3, 4], mechanical alloying [5-9], plasma processing [2, 10] and vapor deposition [2, 11] have been receiving serious attention from researchers.

The central underlying theme in all these techniques is to synthesize materials in a non-equilibrium state by ``energizing and quenching''. The energization involves bringing the materials into a highly non-equilibrium (metastable) state by some external dynamical forcing, e.g., through melting, evaporation, irradiation, application of pressure or storing of mechanical energy by plastic deformation [12]. Such materials are referred to as “driven materials'' by Martin and Bellon [13] (shown in Fig. 2.1).

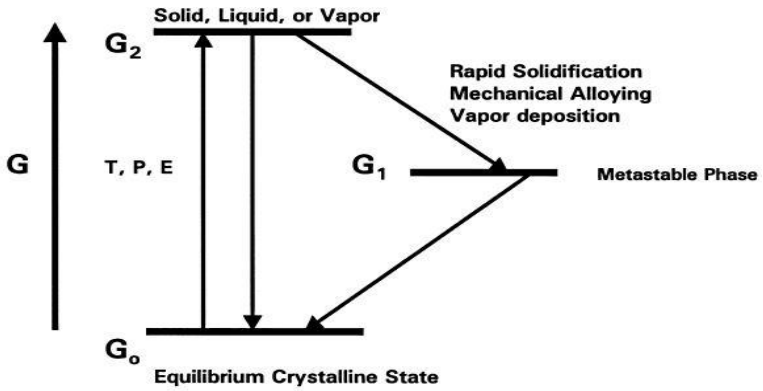


Fig. 2.1: The basic concept of “energizing and quenching” to synthesize non-equilibrium particles. [1]

Mechanical alloying (MA) is a solid-state powder processing technique involving repeated welding, fracturing, and re-welding of powder particles in a high-energy ball mill [1]. It is a fundamentally different approach to alloy manufacture than traditional techniques which use heat treatments and chemical reactions to combine alloy components as it mainly relies on deformation processes to mix materials. So, deformation taking place is an integral part of the MA process. Treated powders are mixed together in a ball milling machine. The powder particles get trapped between the powders as shown in the Fig. 2.2 which causes their deformation and mixing.

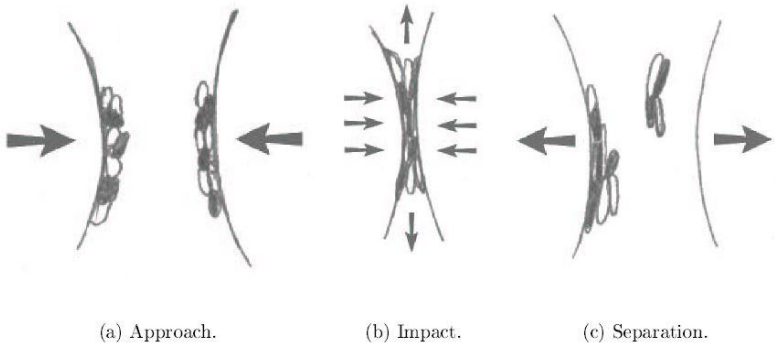


Fig. 2.2: Kneading of powder as milling media collide. [25]

2.1 Process of MA:

The most important components in MA are as following:

- Raw Materials
- Mill variables
- Process variables

The process of MA starts with mixing of the powders in the required proportion and loading the powder mix into the mill along with the grinding medium (generally steel balls). The mix obtained is then milled for the desired length of time until a steady state is reached. Steady state is the state when the composition of every powder particle is the same as the proportion of the elements in the starting powder mix. The milled powder is then consolidated into a bulk shape and heat treated to obtain the desired microstructure and properties.

2.1.1 Raw Materials:

Generally raw materials with particle sizes in the range of 1-2000mm are used for MA. The powder particle size decreases exponentially with time and reaches a small value of a few microns only after a few minutes of milling. So, powder particle size is not very critical, except that it should be smaller than the grinding ball size.

The raw powders fall into the broad categories of pure metals, master alloys, pre-alloyed powders and refractory compounds. Dispersion strengthened materials usually contain additions of carbides, nitrides, and oxides. Oxides are the most common and these alloys are known as oxide-dispersion strengthened (ODS) materials.

Earlier, the powder charge always consisted of at least 15 vol% of a ductile compressible deformable metal powder to act as a host or a binder. However, in recent years, mixtures of fully brittle materials have been milled successfully resulting in alloy formation [5]. Thus, the requirement of having a ductile metal powder during milling is no longer necessary. Hence, ductile-ductile, ductile-brittle and brittle-brittle powder mixtures are milled to produce novel alloys.

Sometimes, metal powders are milled with a liquid medium and this is referred to as wet grinding [14-16]. If no liquid is involved then it is referred to as dry grinding. Another kind of wet milling is Cryo-milling, where the liquid used is at cryogenic temperature. In case of wet grinding the solvent molecules are adsorbed on the newly formed surfaces of the particles and lower their surface energy. So, wet grinding is better method than dry grinding to obtain finer-ground products. The less-agglomerated condition of the powder particles in the wet condition is also a useful factor. Moreover, it has been reported [17] that the rate of amorphization is faster during wet grinding than during dry grinding. But, the disadvantage of the wet grinding is that an increased contamination of the powder occurs due to the sticking. Thus, most of the MA/MM operations are generally carried out dry.

2.1.2 Types of mills:

Different types of high-energy milling equipment are used to produce mechanically alloyed powders. They differ in their capacity, efficiency of milling and additional arrangements for cooling, heating etc. Some of the mills are:

- SPEX shaker mills
- Planetary ball mills
- Attrition mills
- Commercial mills

2.1.3 Process Variables:

Mechanical alloying is a complex process and hence involves optimization of a number of variables to achieve the desired product phase and/or microstructure. Some of the important parameters that have an effect on the final constitution of the powder are:

- Type of mill
- Milling container
- Milling speed
- Milling time
- Type, size, and size distribution of the grinding medium
- Ball-to-powder weight ratio
- Extent of filling the vial
- Milling atmosphere
- Process control agent
- Temperature of milling

But, all the process variables mentioned above are not completely independent. For example, the optimum milling time depends on the type of mill, size of the grinding medium, temperature of milling, ball-to-powder ratio, etc. The following discussion is based on the assumption that other variables have no significant effect on the specific variable being discussed.

2.1.3.1 Type of mill:

There are a number of different types of mill for carrying out MA. These mills are mainly differing in their speed of operation, capacity and their ability to control the operation by varying the temperature of milling and the extent of minimizing the contamination of the powders. Thus, type of powder, the quantity of powder and the final constitution required decide the type of mill to be used.

Table 1: Typical capacities of the different types of mills [18]

Mill Type	**Sample Weight**
Mixer Mills	Up to 2x20g
Planetary mills	Up to 4x250g
Attritor	0.5-100kg
Uni –ball mills	Up to 4x2000g

2.1.3.2 Milling Container

It is also known as grinding vessel, vial, jar or bowl. During the process of grinding the grinding medium constantly strike on the inner walls of the container and thus can dislodge some material which may join the powder phase. This may contaminate the powder and alter the chemistry of the powder. The shape of the container is also an important parameter, especially the internal design of the container. Both flat

ended and round ended SPEX mill containers are being used these days. It has been found that alloying occur at a significant higher rates in the flat-ended vial than in the round-ended container [19]. Some of the common materials used for the grinding vessels are Hardened steel, tool steel, hardened Chromium steel, tempered steel, stainless steel, WC Co, WC-lined steel [20] and bearing steel.

2.1.3.3 Milling speed

The Faster the mill rotates the higher would be the energy input into the powder. But, depending on the design of the mill there are certain limitations on the maximum speed that could be employed. For example, in a conventional ball mill increasing the speed of rotation will increase the speed with which the balls move. Above a critical speed, the balls will be pinned to the inner walls of the vial and do not fall down to exert any impact force. Therefore, the maximum speed should be just below this critical value so that the balls fall down from the maximum height to produce the maximum collision energy. Another limitation to the maximum speed is that at high speeds (or intensity of milling), the temperature of the vial may reach a high value. This may be advantageous in some cases where diffusion is required to promote homogenization and/or alloying in the powders. But, in some cases, this increase in temperature may be a disadvantage because the increased temperature accelerates the transformation process and results in the decomposition of supersaturated solid solutions or other metastable phases formed during milling [21]. Additionally, the high temperatures generated may also contaminate the powders. It has been reported that during nano-crystal formation, the average crystal size increases and the internal strain decreases at higher milling intensities due to the enhanced dynamical recrystallization [22]. The maximum temperature reached is different in different types of mills and the values vary widely.

2.1.3.4 Milling time

The time of milling is the most important parameter. Normally the time is so chosen as to achieve a steady state between the fracturing and cold welding of the powder particles. The times required vary depending on the type of mill used, the intensity of milling, the ball-to-powder ratio, and the temperature of milling. These times have to be decided for each combination of the above parameters and for the particular powder system. But, it should be realized that the level of contamination increases and some undesirable phases form if the powder is milled for times longer than required [23]. Therefore, it is desirable that the powder is milled just for the required duration and not any longer.

2.1.3.5 Grinding medium

Some of the commonly used grinding medium are hardened chromium steel, tempered steel, stainless steel, WC Co and bearing steel. The density of the grinding medium should be high enough so that the balls create enough impact force on the powder [1]. It is always desirable, whenever possible, to have the grinding vessel and the grinding medium made of the same material as the powder being milled to avoid cross contamination [1]. The size of the grinding medium also has an influence on the milling efficiency. Generally speaking, a large size (and high density) of the grinding medium is useful since the larger weight of the balls will transfer more impact energy to the powder particles.

2.1.3.6 Ball to powder ratio

The ratio of the weight of the balls to the powder (BPR), sometimes referred to as charge ratio (CR), is an important variable in the milling process. This has been varied by different investigators from a value

as low as 1:1 [24] to as high as 220:1 [120]. Generally speaking, a ratio of 10:1 is most commonly used while milling the powder in a small capacity mill such as a SPEX mill. But, when milling is conducted in a large capacity mill, like attrition, a higher BPR of up to 50:1 or even 100:1 is used. The BPR has a significant effect on the time required to achieve a particular phase in the powder being milled. The higher the BPR, the shorter is the time required. At a high BPR, because of an increase in the weight proportion of the balls, the number of collisions per unit time increases and consequently more energy is transferred to the powder particles and so alloying takes place faster. Several other investigators also have reported similar results. It is also possible that due to the higher energy, more heat is generated and this could also change the constitution of the powder. The amorphous phase formed may even crystallize if the temperature rise is substantial.

2.1.3.7 Extent of filling the vial

Since alloying among the powder particles occurs due to the impact forces exerted on them, it is necessary that there is enough space for the balls and the powder particles to move around freely in the milling container. Therefore, the extent of filling the vial with the powder and the balls is important. If the quantity of the balls and the powder is very small, then the production rate is very small. On the other hand, if the quantity is large, then there is not enough space for the balls to move around and so the energy of the impact is less. Thus, care has to be taken not to overall the vial; generally about 50% of the vial space is left empty.

2.1.3.8 Milling atmosphere

The major effect of the milling atmosphere is on the contamination of the powder. Therefore, the powders are milled in containers that have been either evacuated or filled with an inert gas such as argon or helium. (Nitrogen has been found to react with metal powders and consequently it cannot be used to prevent contamination during milling, unless one is interested in producing nitrides.) High-purity argon is the most common ambient to prevent oxidation and/or contamination of the powder. It has also been noted that oxidation can be generally prevented or minimized in the presence of nitrogen ambient.

2.1.3.9 Process control agents

The powder particles get cold-welded to each other, especially if they are ductile, due to the heavy plastic deformation experienced by them during milling. But, true alloying among powder particles can occur only when a balance is maintained between cold welding and fracturing of particles. A process control agent (PCA) (also referred to as lubricant or surfactant) is added to the powder mixture during milling to reduce the effect of cold welding. The PCAs can be solids, liquids, or gases. They are mostly, but not necessarily, organic compounds, which act as surface-active agents. The PCA adsorbs on the surface of the powder particles and minimizes cold welding between powder particles and thereby inhibits agglomeration. The surface-active agents adsorbed on particle surfaces interfere with cold welding and lower the surface tension of the solid material. Since the energy required for the physical process of size reduction, E is given by

$$E=\Upsilon.\Delta s$$

Where, 'ϒ' is the specific surface energy and 'Δs' is the increase of surface area, a reduction in surface energy results in the use of shorter milling times and/or generation of finer powders.

2.1.3.10 Temperature of milling

The temperature of milling is another important parameter in deciding the constitution of the milled powder. Since diffusion processes are involved in the formation of alloy phases irrespective of whether the final product phase is a solid solution, intermetallic, nanostructure, or an amorphous phase, it is expected that the temperature of milling will have a significant effect in any alloy system. There have been only a few investigations reported where the temperature of milling has been intentionally varied. This was done by either dripping liquid nitrogen on the milling container to lower the temperature or electrically heating the milling vial to increase the temperature of milling. These investigations were undertaken to study the effect of milling temperature on the variation in solid solubility levels, or to determine whether an amorphous phase or a nano-crystalline structure forms at different temperature.

2.2 Stages of MA

Benjanim and Volin [26] have identified five different stages of alloying:

2.2.1 Particle flattening

This is the first stage of milling and initially the particles get flattened and become flake like.

2.2.2 Welding predominance

During the second stage the flattened particles weld to form lamellar or layered composite particles.

2.2.3 Equiaxed particle formation

After this, the lamellar particles cease to be flake like and become thicker and rounded. The shape change is caused by the work hardening of the powders.

2.2.4 Random welding orientation

Welding of particles again starts as the fragments from the Equiaxed particles start to weld in different orientations and the lamellar structure starts degrading.

2.2.5 Steady state processing

Ultimately, the structure of the material gets gradually refined as fragments are taken from the particles that later weld with other fragments in different orientations.

Particles of each of these five stages are shown in Fig. 2.3.

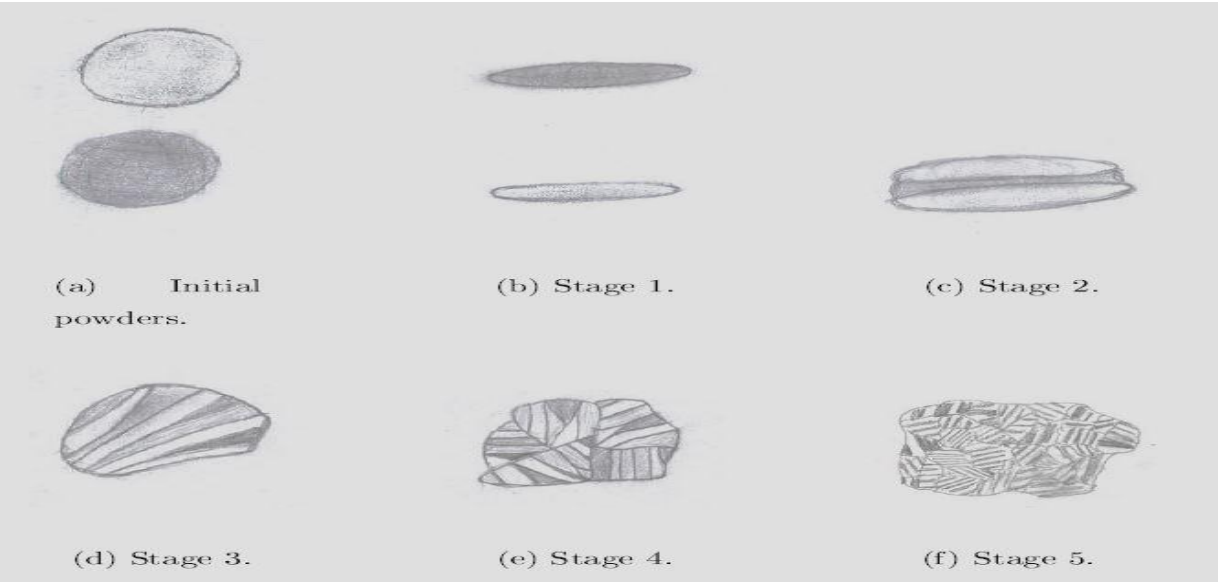


Fig. 2.3: The five stages of Mechanical alloying described by Benjamin and Volin. [25, 26]

2.3 Mechanical alloying of Aluminium base alloys

Development of super alloys by mechanical alloying with advanced mechanical properties and success in their processing led to introduction of this method in dispersion strengthened aluminum alloys also. Presence of aluminum oxide layer on the surface of powder particles during milling or at the start of the processing always enhances improvement in the alloy properties. Aluminum is a ductile material as we know; cold welding during milling is minimized by using an appropriate PCA. Stabilization of grain refinement occurs with the presence of oxide and carbide (formed during milling by the decomposition of the PCA) type dispersions of finer size. As much as up to 50 % improvement in Strength, fracture toughness and corrosion resistance is possible with the stabilization of grain refinement [1].

2.4 Consolidation of mechanically alloyed powder

The production of powder containing a dispersion of reinforcements like SiC, TiO_2, Al_2O_3 in Al-4.5%Cu matrix is only the first step in achieving the complete potential of dispersion hardened Al alloys. The powders produced must be consolidated and then sintered or heat treated to develop coarse grains. So, as a thumb rule MA powder is always consolidated and heat treated to optimize grain structure and properties. But, the consolidation should be done in such a way that it doesn't lead to any inhomogeneity in the matrix. During sintering grain growth is inevitable but it should in an optimum amount only. This is because despite of improving creep resistance it may lead to a less ductility and strength.

3. Experimental Details

This chapter begins with a brief description of sample history. Three different alloy compositions were synthesized by Mechanical Alloying and have been used for the present study. After the description of sample history, mechanical alloying, compaction and sintering, equipment and techniques utilized for characterization of the three alloys systems have been systematically narrated.

3.1 Sample History

The alloys were synthesized from elemental powders through mechanical alloying route. Base alloy system includes Aluminium (> 99% pure) and Copper (> 98.7% pure) powders. Further SiC and TiO_2 powders were added as reinforcements by hand mixing. These powders were weighed and blended in appropriate proportion before and after milling. For base alloy preparation ball mill vial was filled with 28.65g of Aluminium powder and 1.35g of Copper powder in the weight percentages of 95.5 and 4.5 respectively. During the milling process toluene was added as a process controlling agent. It helps in reducing the agglomeration of powders during milling. Actually, toluene gets adsorbed on the surface of the powder particles and minimizes cold welding between powder particles and thereby inhibits agglomeration.

After 15 hour of ball milling four different alloy compositions were synthesized by hand mixing of base alloy with SiC (5 and 10 vol. %) and TiO_2 (5 and 10 vol. %) reinforcements which are summarized in table 3.1.

Table 3.1: Composition of powder blend after mechanical alloying

Powder	Al (wt. %)	Cu (wt. %)	SiC (vol. %)	TiO_2 (vol. %)
Base Alloy	95.5	4.5	0	0
Alloy A	95.5	4.5	10	0
Alloy B	95.5	4.5	5	0
Alloy C	95.5	4.5	0	10
Alloy D	95.5	4.5	0	5

3.2 Mechanical alloying

Aluminium and Copper powders were subjected to milling in a bivial planetary ball mill operated at 300rpm using stainless steel container and balls (10 mm diameter) to produce Al–4.5 wt% Cu alloy powder. A wet medium (toluene) was used, with a ball to powder ratio of 10:1. The milling was performed in manual mode i.e. 30 minutes of milling followed by pause mode for another 30 minutes. Optimization of milling parameters was done through several preliminary attempts on different powder blends. As mentioned earlier, toluene was added to avoid agglomeration of powders during milling, prevent undue oxidation and ensure sufficient yield after the completion of milling.

Table 3.2: Milling parameters adopted

Parameter	**Value**
Balls/powder ratio	10:1
Ball diameter	5 mm
Atmosphere	Air
PCA	Toluene
Weight of powder	30g
Grinding medium	Cr steel
Milling time	15 h(pause mode every 30 min)
Type of mill	Planetary mill
Milling speed	300rpm

Samples of the milled powders were collected at different milling times: 0, 2, 7, 11 and 15 h.

3.3 Compaction and Sintering

After alloying the powders were cold compacted in a hydraulic compressor with a weight of 12.45 tonnes to form round disk specimens of 3mm thickness and 15mm in diameter. For compaction five different kinds of powders were selected as mentioned in Table 3.1. The milled powder was filled in the cylindrical shaped die, loaded in the isotactic hydraulic compressor and pressure was gradually

increased to 12.44 tonnes. The disk shaped sample was then unloaded manually. To ensure the smooth removal of specimen after lubricating agent was used.

The pellets obtained after compression were sintered in a furnace at 550°C for 1 hour. Argon gas at a pressure of 10^{-6} tor was blown inside the furnace to generate an inert atmosphere to protect the pellets against oxidation and any other undue chemical reactions.

3.4 Characterization of mechanically alloyed powders and sintered pellets

The mechanically alloyed powders were analyzed by X-Ray Diffraction, SEM to understand the topographical characteristics and get information about elements and phases present in the powder after different hours of milling as mentioned earlier. XRD and SEM of sintered samples were also carried out in order to understand the effect of temperature and compression on the elements and phases present in the alloy synthesized.

3.4.1 X- Ray Diffraction analysis

X-ray diffraction (XRD) studies were carried out for the purpose of identity and phase evolution at different stages of milling and also after sintering by using the Cu-Kα radiation (having wavelength of 0.1789 nm) in a Phillip's X'pert PRO high resolution X-ray diffratometer. The X-ray source was operated at a voltage of 40 kV and current of 35 mA. The diffraction angle was varied in the range of 20-100 degrees while the scanning rate was 0.05degree/s. The XRD data diffraction patterns were analyzed with the help of Phillip's X'pert software. The crystallite size and lattice strain were estimated by measuring the broadening of the X-ray peaks by using Williamson- Hall plot.

Fig. 3.1: Philips X-pert MPD X-ray diffractometer

3.4.2 Scanning electron microscopy

Microstructure characterization, morphology and particle size determination was carried by a JEOL JSM-6480 LV scanning electron microscope. Both the secondary electron (SE) mode and back scattered electron mode (BSE) were used as per the requirement. To carry out the compositional analysis of the alloy powders EDX of selected areas of the specimen was done with an attached JEOL JSM-6480 LV EDX with the SEM.

Fig. 3.2: JEOL JSM-6480LV scanning electron microscope.

3.5 Hardness measurement

To reveal the mechanical properties of the synthesized material micro-hardness measurement was carried out in a micro-hardness tester. Hardness studies of compact sintered samples were carried out by using Vickers micro hardness tester. For that sample preparation was done primarily by using 1/0, 2/0, 3/0 and 4/0 emery papers there after cloth polishing was done. Hardness was measured on all the samples using Wolpert Vickers hardness tester. Loads of 100g for dwell time of 10seconds and a square base diamond pyramid indenter with an included angle of 360° between the faces were used during hardness measurement. As a result of the indenter's shape, the impression on the surface of the specimen was a square. The length of the diagonals of the square was measured through a microscope fitted with an ocular micrometer. Machine itself displays the hardness value in Vickers Pyramid Number (HV) or Diamond Pyramid Hardness (DPH). A minimum of 3 readings were taken on each sample and checked for consistency.

4. Results and Discussion

4.1 X-Ray Analysis:

4.1.1 General Interpretation of diffraction patterns

Figure 4.1 depicts XRD pattern and their analysis of five samples which are base alloy milled at 0, 5, 7, 11 and 15 hours respectively. It is revealed from the peak analysis that Al and Cu are present during the initial stage of milling. Various interesting observations can be obtained from these diffraction patterns for the structural characterization of the powder at different stages of milling.

The first and the most interesting observation is that the Al peaks tend to broaden as milling time increases. According to the Scherer's formula we know that as crystallite size decreases peak tends to broaden. So it can be inferred that the Al crystallite size decreases as milling time increases.

Secondly, the Cu peaks, which were clearly visible after 2 h of milling, disappeared after 7 h of milling. The reduction and disappearance of the Cu peaks in the XRD patterns is coherent with the disappearance of the Cu contrast observed in the SEM analysis. The disappearance of Cu peaks reveals that Cu is getting diffused inside the Al lattice to form a solid solution which is the fundamental step of alloying.

At the bottom of the figure 4.1 diffraction pattern obtained after sintering at 550°C for 1 hour is shown. Several new peaks can be seen which are due to the formation of Al_2Cu. Moreover there is not much peak broadening or decrease in intensity of Al peaks on heating to 550°C which shows that crystallite size remains same.

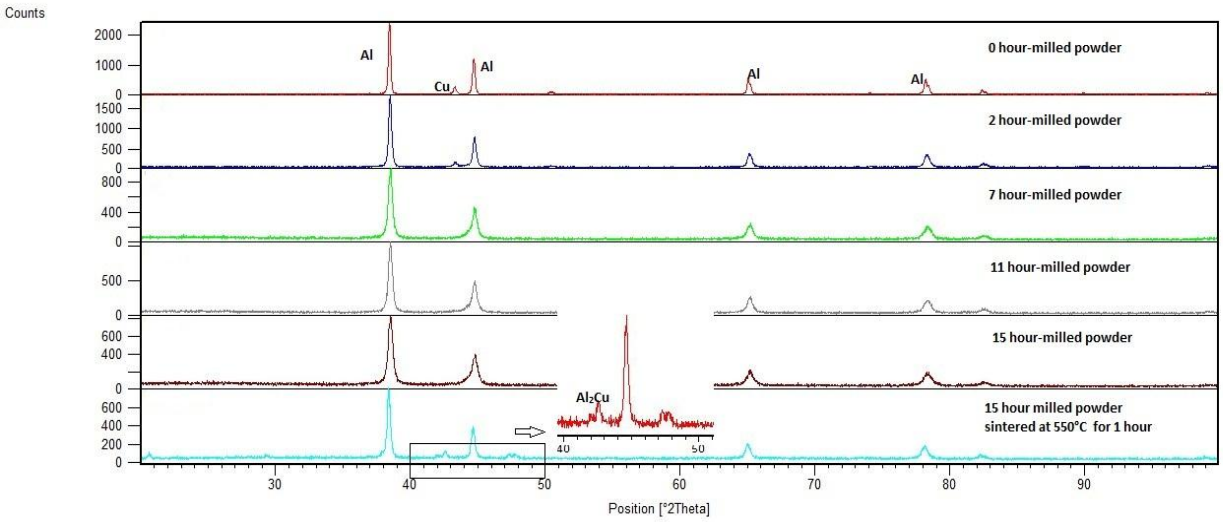


Fig. 4.1: XRD results of base alloy powder samples at different milling hours

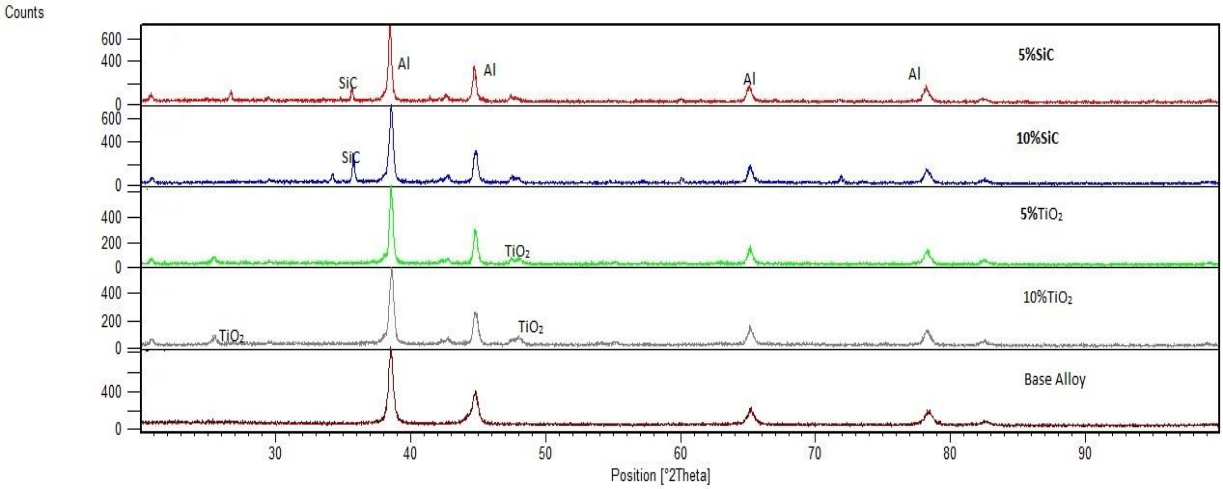


Fig. 4.2: XRD results of compact sintered pellets with different vol percentages of reinforcements

The above figure 4.2 shows that the addition of SiC or TiO_2 decreases the intensity of Aluminium peaks because of the mutual diffusion of Aluminium and Copper. It also shows that the elemental diffusion of Aluminium and Copper increases with addition of SiC and TiO_2, Also the elemental diffusion increases with increase in the concentration of SiC and TiO_2. The decrease in intensity of Aluminium peaks is greater in case of SiC as compared to TiO_2 which shows that the rate of diffusion is greater when SiC is added. The peak broadening increases with the addition or increment in the concentration of SiC and TiO_2. This shows that crystallite size decreases and the lattice strain increases causing an increase in the defect density.

4.1.2 Crystallite size and lattice strain calculation:

The peak broadening of the Aluminium can be attributed to various factors like instrumental error, crystallite size and microstrain. For calculating the crystallite size William –Hall method [28] was used. It is assumed that the line broadening due to the crystallite size follows the Scherer's formula:

$$\beta_t = \frac{0.9\lambda}{D\cos\theta} \qquad (4.1)$$

Here 'D' is Crystallite size, 'λ' is wave length of X-Ray (0.1541 nm), 'β_t' is FWHM (full width at half maximum due to crystallite size) and 'θ' is the diffraction angle. [27] Also the line broadening due to microstrain is given by the Wilson formula:

$$\beta_s = 4\varepsilon tan\theta \qquad (4.2)$$

Here, 'ε' is the root mean square value of microstrain, 'β_s' is FWHM (full width at half maximum due to microstrain) and 'θ' is the diffraction angle.

For calculating the crystallite size and lattice strain it is assumed that the line broadening due to the crystallite size and microstrain are independent of each other and both have a Cauchy like profile[28] i.e. the observed line breadth is simply the linear sum 'β_t' and 'β_s'.

$$i.e.\ \beta = \beta_t + \beta_s \qquad (4.3)$$

$$i.e.\ \beta cos\theta = \frac{0.9\lambda}{D} + 4\varepsilon sin\theta \qquad (4.4)$$

The above equation is the Williamson-Hall equation. Now to calculate the crystallite size and the lattice strain '$\beta cos\theta$' is plotted against '$4sin\theta$'. The slope of the straight line obtained on plotting will give the lattice strain and the crystallite size can be calculated from the intercept. The present Williamson-Hall is based on the uniform deformation model i.e. the crystal structure is considered to be isotropic so that microstrain 'ε' is assumed to be uniform in all the crystallographic directions.

Table 4.1 Calculation of average crystallite size and lattice strain

At 0h:

Peak position,2 θ	**βcosθ**	**4sinθ**
38.41	3.13×10^{-3}	1.3158
44.66	3.87×10^{-3}	1.5197
65.03	4.71×10^{-3}	2.1500
78.17	4.87×10^{-3}	2.5220
Average crystallite size=53.34nm	**Lattice strain(ε)=0.06%**	

At 2h:

Peak position,2 θ	**βcosθ**	**4sinθ**
38.41	4.12×10^{-3}	1.3158
44.66	4.68×10^{-3}	1.5197
65.03	6.62×10^{-3}	2.1500
78.17	6.50×10^{-3}	2.5220
Average crystallite size=43.34nm	**Lattice strain(ε)=0.09%**	

At 7h:

Peak position,2 θ	**βcosθ**	**4sinθ**
38.41	6.26×10^{-3}	1.3158
44.66	7.10×10^{-3}	1.5197
65.03	7.94×10^{-3}	2.1500
78.17	10.50×10^{-3}	2.5220
Average crystallite size=30.84nm	**Lattice strain(ε)=0.10%**	

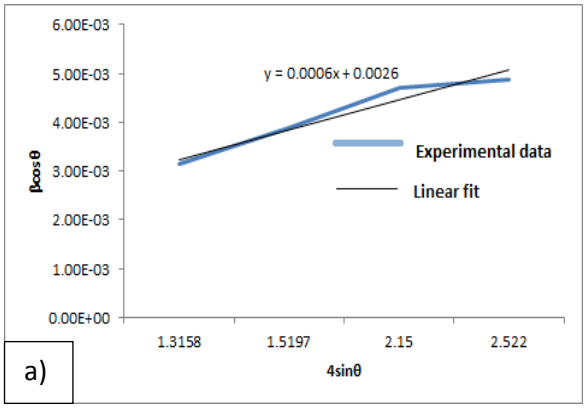
At 11h:

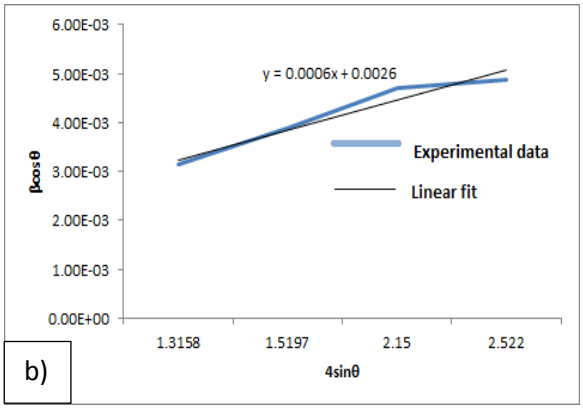
Peak position,2 θ	**βcosθ**	**4sinθ**
38.41	6.26×10^{-3}	1.3158
44.66	7.42×10^{-3}	1.5197
65.03	7.79×10^{-3}	2.1500
78.17	10.15×10^{-3}	2.5220
Average crystallite size=28.30nm	**Lattice strain(ε)=0.12%**	

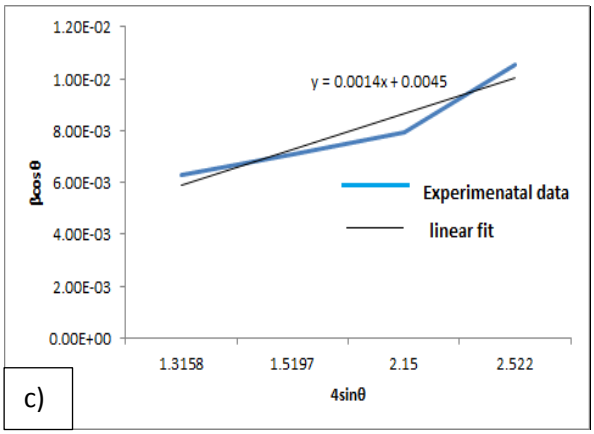
At 15h:

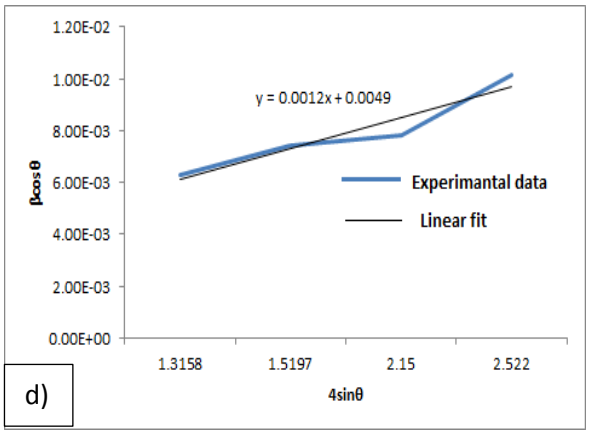
Peak position,2 θ	βcosθ	4sinθ
38.41	6.59×10^{-3}	1.3158
44.66	8.34×10^{-3}	1.5197
65.03	9.86×10^{-3}	2.1500
78.17	10.55×10^{-3}	2.5220

Average crystallite size=25.22nm **Lattice strain(ε)=0.13%**









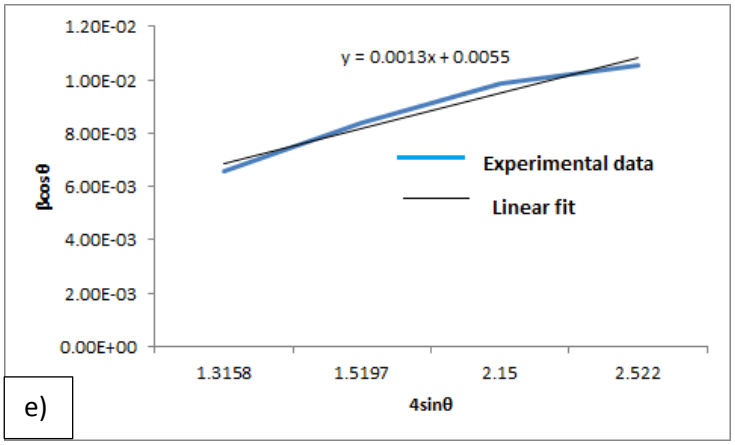


Fig. 4.3 Calculation of average crystallite size and lattice strain at (a) 0h, (b) 2h, (c) 7h, (d) 11h and (e) 15h of milling.

The following graph clearly illustrates that the crystallite size decreases as milling time increases. Moreover the rate of decrease of the crystallite size also decreases with milling time. This is because there is a tendency of the particle size to reach an equilibrium value as milling time increases. Actually steady state equilibrium is reached when there is a balance between the rate of welding, which tends to increase the particle size, and the rate of fracturing, which tends to decrease the average composite particle size [1].

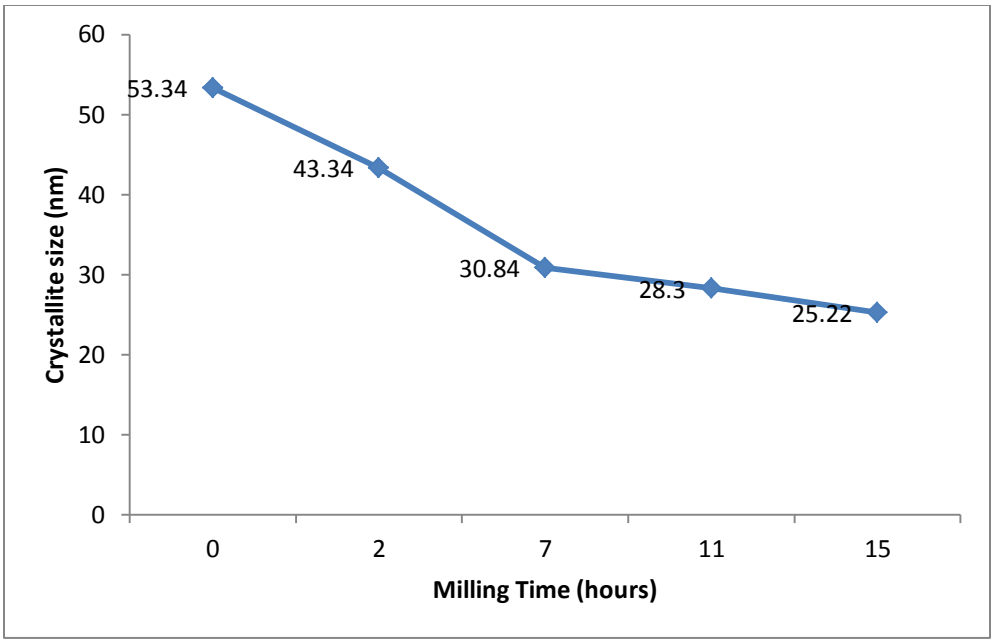


Fig. 4.4: Crystallite size as a function of milling time.

The following graph shows that the lattice strain increases with extent of milling. This is due to the crystallite refinement occurring because of the mechanical deformation during milling.

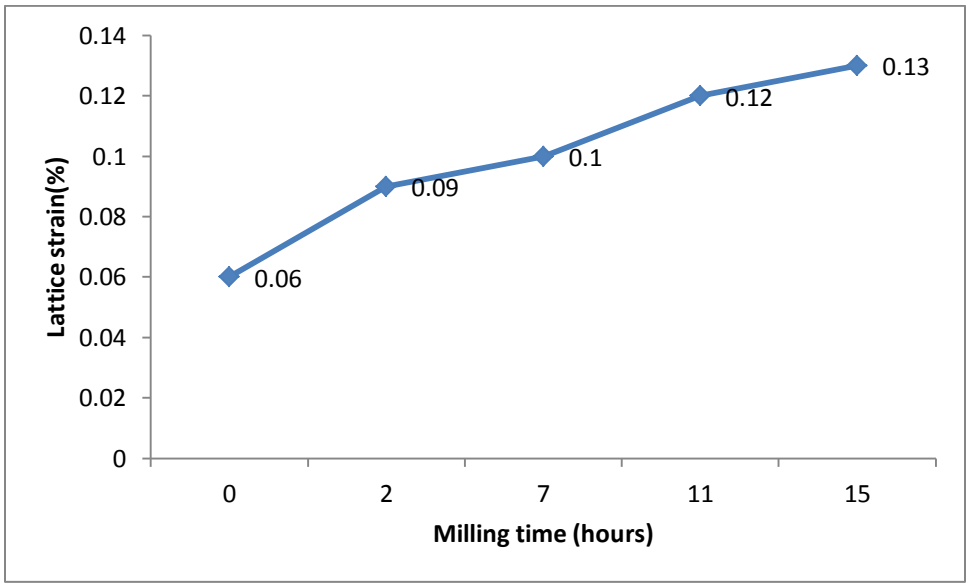
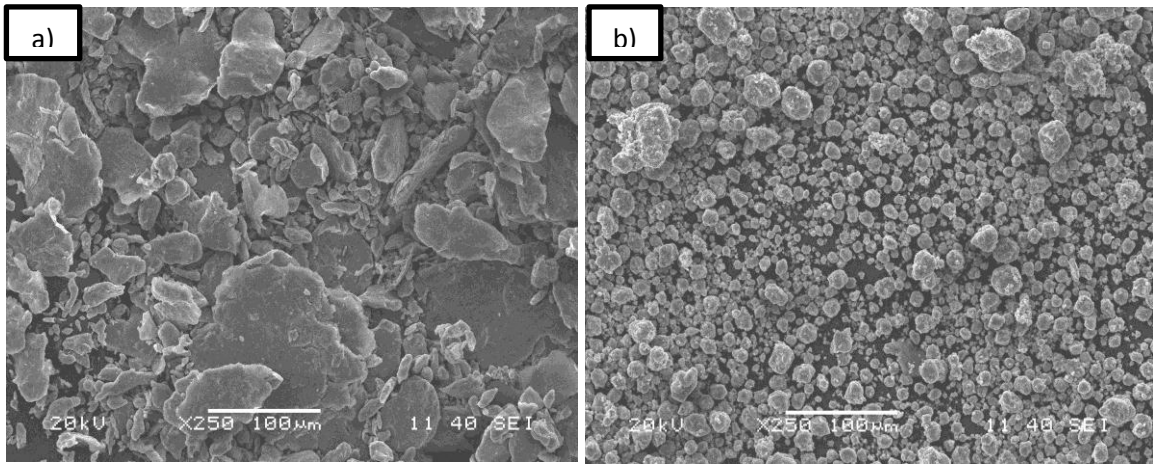


Fig. 4.5: Lattice strain as a function of milling time

4.2 SEM Analysis:

4.2.1 Morphology Analysis

Figure.4.6 (a, b, c) shows the microstructure of mechanically alloyed Al-4.5%Cu powders after 0, 11 and 15 hours of milling. The brighter Copper phase can easily be differentiated from darker Aluminium phase. As we know that during mechanical alloying continuous cold welding, fracturing and re-welding of particles take place. This fact is well illustrated in the following micrographs. After 11 hours of milling several laminar and coarser Copper particles have welded and as the milling was continued further these laminar shaped particles have transformed to equiaxed grains. The disappearance of brighter Copper phase from the micrograph, as the milling is continued, shows that Copper is getting diffused inside the Aluminium lattice. The Copper contrast soon disappeared as milling was continued. It is clear from the micrographs that the crystallite size of the alloy is decreasing with milling time and it is also supported by the XRD results as mentioned above in the X-ray analysis.



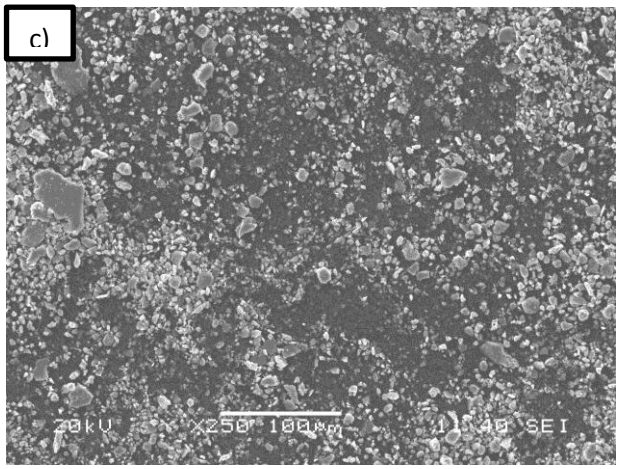


Fig. 4.6: SEM images of Al-4.5% Cu powders milled for a) 0 hr; b) 11 hr and c) 15 hr.

The following figure shows that SiC and TiO_2 have appropriate distribution in the matrix. Comparing the content of Copper in the base alloy and reinforced samples it can be said that alloying process has been enhanced on adding the reinforcements.

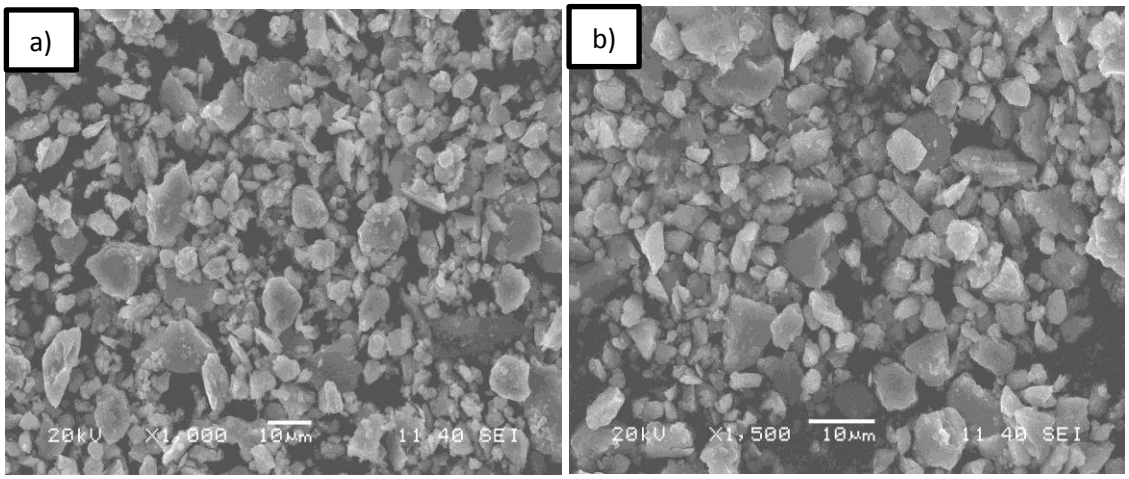


Fig. 4.7: SEM images of a) base alloy+10% SiC; b) base alloy+10% TiO_2.

4.2.2 Compositon Analysis:

Fig. 4.8 shows the Elemental analysis of the base alloy after 15 hour of milling, which was carried out ot investigate the chemical composition of the base alloy powder. The EDX confirms the presence of Al and Cu and some minor impurities such as carbon and oxygen. The EDX analysis results of base alloy with 10 vol.% SiC and base alloy with 10 vol. % TiO_2 powders after 15 h of milling are shown in Fig. 4.9 and Fig. 4.10 which confirms the presence of Si and Ti. Presence of carbon in the chemical composition is due to usage of carbon conducting material during analysis.

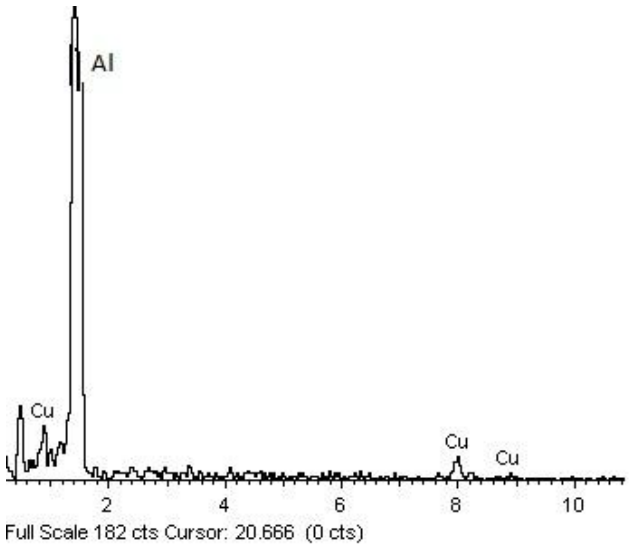


Fig. 4.8: EDX results of base alloy after 15 hr milling.

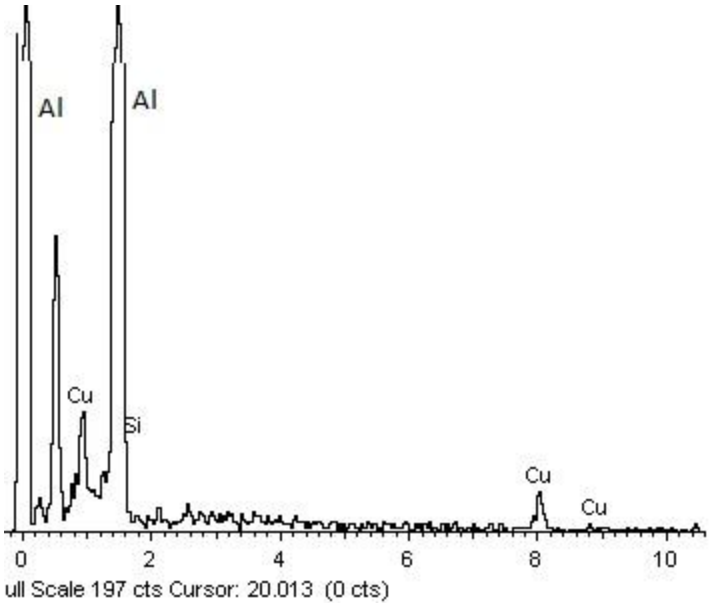


Fig. 4.9: EDX results of base alloy after 15h milling with 10% SiC.

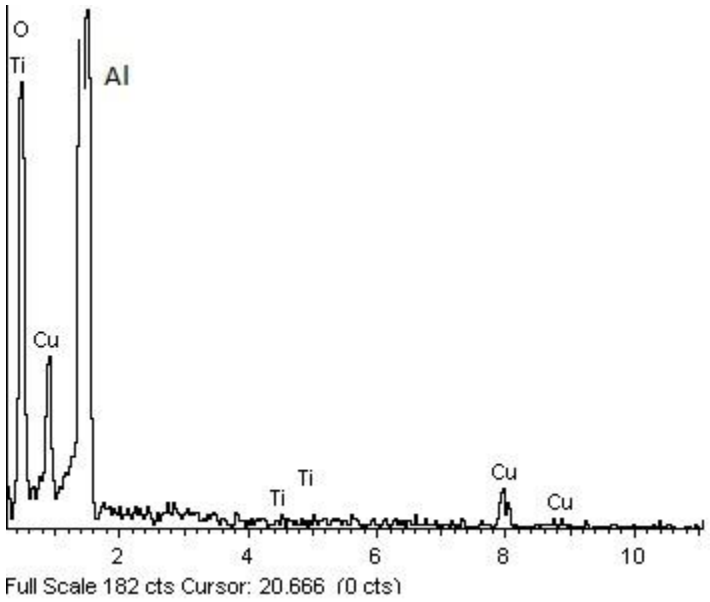


Fig. 4.10: EDX results of base alloy after 15h milling with 10% TiO_2.

4.3 Hardness study:

Advancement in mechanical properties during mechanical alloying of Al-4.5%Cu is due to the solid solution strengthening. Further finer precipitation of SiC and TiO_2 causes dispersion hardening in the Al-4.5%Cu matrix. Hardness and strength are generally analogous properties for any material. This is even more pronounced in case of ductile materials.

Alloy system	1st reading (HV)	2nd reading (HV)	3rd reading (HV)	4th reading (HV)	Average hardness(HV)
Base alloy	155.57	139.83	170.30	140.56	151.56
Base alloy+5%TiO_2	203.70	188.68	193.42	209.58	198.84
Base alloy+10% TiO_2	217.62	222.43	197.08	231.90	217.25
Base alloy+5%SiC	209.04	193.71	218.35	211.27	208.09
Base alloy+10%SiC	237.16	225.92	239.18	210.34	228.15

The hardness increases with addition of SiC and TiO_2. Moreover, increase in the hardness is greater in case of SiC. This is also supported by the XRD result which shows that the rate of diffusion of elemental Al and Cu is more when we add SiC.

4.4 Discussion

The mechanical strength of the present alloys can be interpreted by various strengthening mechanisms such as dispersion hardening, solid solution hardening and grain refinement (Hall–Petch effect)[29]. Due to the sintering of these alloys at high temperature grain coarsening must have taken place and can't be neglected. So it is anticipated that strengthening effect due to grain refinement even if present in the as milled condition can't be considered after sintering. So strengthening due to dispersion and solid solution effects would dominate over grain refinement effect.

Dispersion strengthening in the current SiC or TiO_2 reinforced alloy is primarily based on the volume fraction, particle size and inter-particle spacing of fine SiC and TiO_2 the matrix. Beside, in situ Al_2Cu particles have also been detected in the sintered microstructure. The size and distribution of these fine phases are determined by nucleation, growth and coarsening rates during sintering.

5. Summary and Conclusion

The present study encompasses a precise and detailed microstructural characterization and mechanical property evaluation of five different alloys synthesized via. Mechanical Alloying and consolidated at 550°C for 1 hour in Argon atmosphere. These alloys differ in concentration of SiC and TiO_2. The important conclusions that can be drawn from the results presented here are as following:

- It is possible to synthesis Al-4.5%Cu alloy by mechanical alloying and uniformly dispersed reinforcements such as SiC (5 and 10 vol. %) and TiO_2 (5 and 10 vol. %) in the matrix.
- As the milling time increases particle size decreases up to 11 hours of milling and then becomes nearly constant afterwards. This is because after a certain interval of time steady state equilibrium is attained between the rate of welding and the rate of fracturing. Welding tends to increase the average particle size while fracturing tends to decrease it.
- It is found that the particle size of alloy powder synthesized goes to the nanometric range as observed during XRD and SEM studies.
- Crystallite size decreases and the lattice strain increases with increase in the extent of milling.
- The current alloy follows solid solution strengthening, precipitation hardening and grain refinement.
- There is a 1-1.5 times improvement in hardness value as compared to that of the conventional Al based alloys.

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